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Dynamics of magnetic and electric parameters transformation in thin films of sodium-doped lanthanum manganites

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Transformation dynamics of magnetic and electric parameters in thin films of sodium-doped lanthanum manganite has been studied. The peculiar feature of the films is wide temperature range of the coexistence of ferromagnetic and paramagnetic phases. It has been found that the anomalies on temperature dependences of magnetization, electric resistance and magnetoresistance are shifted relative to each other contrary to the case of doped manganite single crystals, in which such anomalies are observed at almost the same temperature. Based on the magnetic measurements data and theoretical calculations, the dependence of ferromagnetic phase volume fraction V_{FM} on the temperature has been calculated. V_{FM} values have been calculated whereby maximums on temperature dependences of electric resistance and magnetoresistance have been observed. Conclusions have been formulated concerning the shape of ferromagnetic nuclei in the films under consideration.

Исследована динамика трансформации магнитных и электрических параметров в тонких пленках замещенных натрием манганитов лантана, характерной особенностью которых является широкая температурная область сосуществования ферромагнитной и парамагнитной фаз. Обнаружено, что аномалии на температурных зависимостях намагниченности, электрического сопротивления и магнитосопротивления сдвинуты одна по отношению к другой, в отличие от монокристаллических образцов замещенных манганитов, в которых такие аномалии наблюдаются практически при одной и той же температуре. Исходя из данных магнитных измерений и результатов теоретических расчетов, рассчитана зависимость объемной доли ферромагнитной фазы V_{FM} от температуры. Найдены конкретные значения V_{FM}, при которых наблюдаются максимумы на температурных зависимостях электрического сопротивления и магнитосопротивления. Сделаны выводы относительно формы зародышей ферромагнитной фазы в исследуемых пленках.

1. Introduction

$La_{1-x}A_xMnO_3$ doped manganites (where A is an alkaline or alkaline-earth element) are the objects of researchers' attention due to the rich variety of unusual physical properties [1–4]. Metal-semiconductor transition is especially interesting that is usually observed near the transition temperature into ferromagnetic (FM) state and causes colossal magnetoresistance effect. The huge magnetoresistance effect is a very strong (several orders) reduction of electric resistance in manganite materials exposed to an external magnetic field [1, 2]. Mainly due to this effect the thin films of doped manganites are considered as promising materials for a new generation of sensors and magnetic information readout devices [3, 4]. Though the doped manganites are being vigorously studied, the nature of unusual behavior is not yet quite clear [4, 5].

The researches show that in doped manganites the conductivity character is closely related to the magnetic state of these compounds [3, 4]. This results from the fact that *d*-electrons of manganese ions take part in the processes of both charge transfer and magnetic ordering. The presence of manganese ions in various oxidation states (Mn^{3+} and Mn^{4+}) makes charge transfer between these ions possible (by means of the so-called double exchange) only when the magnetic moments of the neighboring ions are parallel to each other, that results in a simultaneous occurrence of ferromagnetism and metallic conductivity [1, 2, 4]. At the same time, a series of other effects (electron-phonon interaction, antiferromagnetic indirect exchange, charge and orbital ordering) prevent from FM ordering and favor localization of charge carriers. If the double exchange prevails over the other interactions, the paramagnetic — ferromagnetic transition and semiconductor — metal one occur practically simultaneously [3, 4, 6]. This leads to the formation of electric resistance peak near the magnetic transition temperature T_C and it is the reason for the strong influence of magnetic field on the conductivity.

In single crystalline samples the temperature of the electric resistance peak (T_R) and T_C practically coincide [3, 6]. In polycrystalline, defective, amorphous and partially crystallized samples such situation is not observed and the temperature difference between T_R and magnetic transition temperature may reach several dozen degrees [7–9]. There are several reasons for such divergence. On the one hand, this is due to the ambiguity of the notion "magnetic transition temperature" in inhomogeneous systems and the difficulty in experimental determination of this physical value. So, in some cases the magnetic transition temperature is understood as the temperature of the nucleation of FM phase, in other — the temperature at which the magnetization change reaches its maximum. On the other hand, the process of the resistance peak formation reflects several different processes, and not all of them are related directly to the magnetic state of doped manganites. It is known that an appearance of the peak on the temperature dependence of resistance reflects the fact that the fraction of the highly conductive phase (in this case FM) reaches a certain value (the so-called percolation threshold V_0), at which an infinite conductive cluster is formed in the system [10]. As it is known from the percolation theory, this value depends not only on the volume fraction of the highly conductive phase, but also on the shape of the conductive regions appearing in a low conductive (in our case paramagnetic (PM)) matrix [10]. It should be noted that the data on behavior of electric resistance and magnetization in transition region for doped manganites with broadened magnetic transition are inconsistent and need refinement [9, 11].

Amorphous and partially crystallized films are convenient objects for studying the processes in the transition region due to relatively wide temperature range of the latter. A width of the transition region can be easily tuned by means of the selection of the film preparation modes [7–12].

In this research sodium-doped lanthanum manganites were chosen as the objects of investigation. The choice is justified by the fact that, on the one hand, sodium introduction into La sublattice may prove useful for enhancement of magnetoresistance properties, particularly, near the room temperature [13–15]. So, in [13] it has been shown that in bulk $La_{1-x}A_xMnO_3$ samples with increase of sodium content the Curie temperature T_C grows and reachs the values exceeding the room temperature. At $x > 0.14$ T_C is practically independent of sodium content. In this concentration region the magnetoresistance is high and may reach 20 % in the fields $H = 15$ kOe at the temperatures over 300 K (for similar strontium-doped lanthanum manganites the values of 7–13 % are typical [3, 16, 17]). On the other hand, in the process of preparation and subsequent thermal treatment of samples sodium evaporates due to its high volatility, thereby structural vacancies create that additionally broaden the transition region [13, 18].

The purpose of the research is to reveal dependence between the dynamics of magnetic and electrical parameter changes in thin films of sodium-doped lanthanum manganites, the peculiarity of which is a wide temperature transitional region from PM to FM state. Since the interest in doped manganites grows, a detailed study of the phenomena in the region of magnetic and resistive transitions is topical. It is necessary to make a generalized picture of the physics of doped manganites without which their practical implementation is impossible. To achieve the purpose electric, magnetic and magnetoresistive measurements were supplemented by resonance ones, which provide

additional information on the magnetic state and magnetic phase composition of the samples with complex magnetic configurations [5, 7, 19].

2. Experimental details

The films of 250 nm thick (hereinafter — LNMO films) were fabricated by means of sputtering of a ceramic target with a nominal composition $La_{0.84}Na_{0.16}MnO_3$ on polycrystalline Al_2O_3 substrates [5, 6]. The target for the film preparation was synthesized by standard solid phase reaction [13, 15, 20]. In this research the studied films were obtained at the substrate temperature T_s = 300°C in argon (30 %) and oxygen (70 %) mixture. Gas medium pressure at the sputtering was $2 \cdot 10^{-2}$ Torr. After being prepared, the films were annealed for 4 h. at T_{ann} = 750°C.

The electric resistance of the films was measured as a function of temperature and magnetic field. The measurements were carried out at direct current by four-probe method using data collection computerized system. The temperature dependences of the electric resistance were obtained during a slow heating of the samples from 120 to 370 K after their preliminary cooling down to the temperature of liquid nitrogen. Magnetoresistance was measured in the fields of up to 15 kOe and defined as $MR = (R_0 - R_H)/R_0$, where R_0 — electric resistance in zero magnetic field, and R_H — in the external field H. The magnetic field was applied in parallel to the film plane and the electric current flow.

The static magnetization was measured in vacuum by Faraday balance [21]. The experiment maximum error did not exceed 2 %. The temperature dependences of the magnetic susceptibility were measured in the range of 120–320 K in the field H = 3 kOe, which is knowingly higher than magnetization saturation field ($H_{sat} \approx 1.5$ kOe at 77 K).

In order to obtain resonance spectra we used RADIOPAN-SE/X-2543 electronic paramagnetic resonance spectrometer with operating frequency ν = 9.2 GHz.

3. Results and discussion

Dependence of magnetization M on temperature T obtained in the field H = 3 kOe for LNMO films is shown in Fig. 1(a). Magnetization increase with temperature decrease becomes noticeable at the temperature values below 290 K. As can be seen

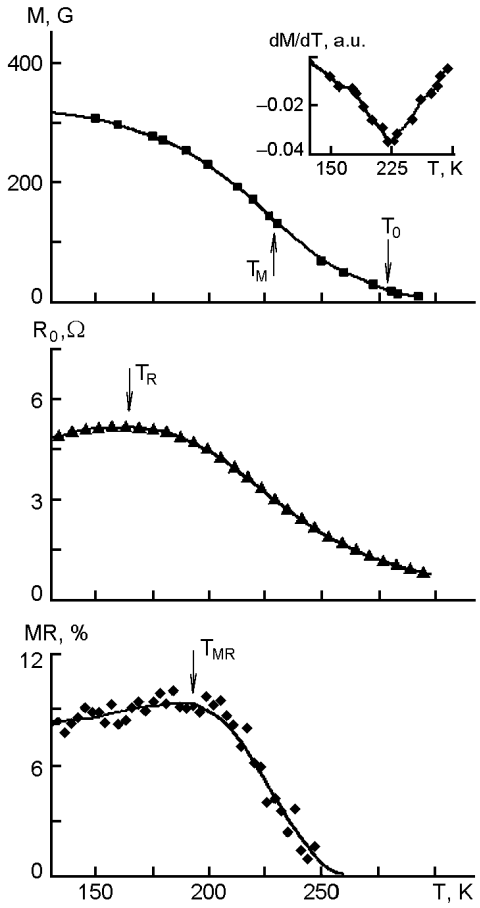

Fig. 1. Temperature dependences of magnetization in the field H = 3 kOe (a), electric resistance (b) and magnetoresistance in 15 kOe field (c) for LNMO film. The inset shows dM/dT dependence as a function of temperature. The figure also shows characteristic temperatures: T_0 — the temperature of FM phase nucleation, determined from magnetic resonance study; T_M — the temperature of the magnetization maximum change; T_R — the temperature at which electric resistance reaches the maximum; T_{MR} — the temperature at which magnetoresistance reaches the maximum.

from the temperature dependences of dM/dT (see inset in Fig. 1), the most dramatic magnetization increase ($|dM/dT|$ = max) is observed at $T_M \cong 227$ K. In the low temperature region the magnetization increase considerably decelerates.

Fig. 1(b) shows the temperature dependence of electric resistance R_0. An appearance of wide maximum on $R_0(T)$ curve is caused by formation of highly conductive FM phase [22, 23]. The maximum electric resistance value is reached at $T_R \cong 166$ K.

Fig. 1(c) shows the temperature dependence of magnetoresistance MR measured in the field $H = 15$ kOe. The field value was chosen high enough to exceed H_{sat}. In the high temperature region an influence of magnetic field on electric resistance is negligibly small ($MR \cong 0$), that is characteristic for PM phase of doped manganites. With the temperature decrease MR increases and reaches the maximum and then slowly decreases with further temperature decrease. The temperature value, at which MR reaches the maximum, T_{MR}, is equal to 190 K. The T_{MR} value exceeds T_R. It is however lower than T_M, which is often observed in doped manganites with increased inhomogeneity [23, 24].

The results of investigating magnetic resonance in LNMO films were given in [25]. It was demonstrated that the resonance signal from FM phase appears at 280 K (T_0 in Fig. 1(a)). Above this temperature the sample is completely paramagnetic, below it the paramagnetic phase coexists with the ferromagnetic in quite a wide temperature range (the presence of PM phase down to 110 K has been confirmed experimentally).

As demonstrated in Fig. 1, the temperature T_R is considerably lower than T_M (the difference is over 60 K), and T_{MR} value is between T_R and T_M. It has been noted above that such relation between the characteristic temperatures can be expected in the systems in which high conductivity FM phase coexists with low conductivity PM phase over a wide temperature range. Similar effects are often observed in doped manganites [26–28], however, as far as we know, there have been no quantitative evaluation of V_{FM} values at which electric resistance or magnetoresistance reach the maximum.

For the films under consideration we have calculated the temperature dependence of the FM phase volume fraction and found the values V_{FM}, which correspond to the characteristic temperatures T_R, T_{MR} and T_M. Assuming that the magnetization of FM phase significantly exceeds that of PM phase. FM phase volume fraction may be calculated by finding the ratio of the experimentally obtained magnetization to the theoretically calculated one.

In the mean field approximation the temperature dependence of the reduced magnetization of FM phase (M_{theor}/M_S) is described by Brillouin's formula [29]:

$$B_j = \frac{2J+1}{2J}\coth\left[\frac{2J+1}{2J}X\right] - \frac{1}{2J}\coth\left[\frac{1}{2J}X\right], \quad (1)$$

where $X = (3J/J+1)\ (T_C/T)\ (M/M_s)$, T_C — Curie temperature, J — total angular momentum and M_s — saturation magnetization at $T = 0$. It was shown in [30, 31] that for doped manganite compounds Brillouin's formula describes the magnetization behavior with a good accuracy.

For doped lanthanum manganites the orbital contribution to the total angular momentum is negligible and J is determined by spin quantum number of Mn ions [30]. Mn ions in these compounds have the oxidation level of 3+ and 4+ with spin quantum numbers $S = 2$ and $S = 3/2$, correspondingly [3, 4]. If Mn^{4+} ion fraction is x, then Mn^{3+} ion fraction is $(1 - x)$, thus, J may be calculated as the weighted total of corresponding quantum numbers:

$$J = x \cdot 3/2 + (1 - x) \cdot 2 \text{ [30].}$$

For $La_{0.84}Na_{0.16}MnO_3$ compound fabricated under the conditions similar to ones used for the samples in this research, the average oxidation state of Mn ions was determined experimentally [13]. The total angular momentum calculated according to these data is $J = 1.64$. In this case the saturation magnetization at $T = 0$ K is 526 G.

The temperature dependence of magnetization calculated by formula (1) is shown in the inset in Fig. 2. Curie temperature was determined based on magnetic resonance data. So, the measurements clearly show a resonance signal from FM phase at 280 K, though at 290 K the sample is completely paramagnetic [25]. Based on these data we have set for calculation that T_C is 285 K.

Fig. 2 gives the plot of the temperature dependence of FM phase volume fraction in LNMO films. It is clearly seen that the abrupt increase of V_{FM} occurs within ~270 K to ~200 K temperature range. The analysis of dependences $M(T)$, $M_{theor}(T)$ and $V_{FM}(T)$ shows that the abrupt increase of M near T_M is a result of the increase in both FM phase volume fraction and its magnetization. It follows from the analysis that the MR and R approach their maximal values in the region where the FM phase fraction exceeds 50 %. So, the electric resistance peak is observed at $V_{FM} \cong 67$ %, while the magnetoresistance peak is observed at $V_{FM} \cong 63$ %. A noticeable magnetoresistance occurs only when the volume fraction of FM phase exceeds 15 %.

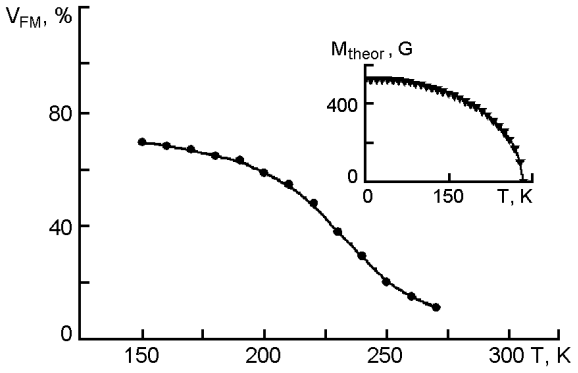

Fig. 2. Temperature dependence of FM phase volume fraction in LNMO film. The inset — temperature dependence of magnetization calculated according to formula (1).

It has been mentioned above that the temperature of electric resistance peak corresponds to the moment when the conductive FM phase volume exceeds the percolation threshold V_0. For the case where conductive regions are spherical calculations of V_0 give values which are close to 30 % (this value depends also on the geometry of conductive sphere arrangement) [10]. For the studied LNMO films this value is 67 %. In our opinion, such fact demonstrates that the shape of the conductive FM regions differs from the spherical one. Additional proofs of this opinion are as follows. First, the magnetic resonance studies reveal a complex character of FM nuclei transformation in the paramagnetic-ferromagnetic transitional region [25]. Second, it is known that in polycrystalline films fabricated by magnetron sputtering crystallites are elongated in the direction perpendicular to the film plane [32]. Obviously, the effect of the shape anisotropy (magnetocrystalline anisotropy in the magnetic transition region usually is quite small) will provide an elongation of the FM nuclei shape in the same direction. Based on the calculation performed in the framework of percolation theory [10] the threshold of percolation may exceed 30 % that is actually observed in this research.

4. Conclusions

Magnetic, electric and magnetoresistance properties of LNMO films have been studied. It has been demonstrated that the temperatures of electric resistance and magnetoresistance maxima significantly differ from each other and from the temperatures at which the anomalies of magnetic properties are observed. Based on the results of magnetic measurements and theoretical calculations the dependence of the FM phase volume fraction V_{FM} on the temperature has been calculated. The values V_{FM} at which maximums on dependences $R_0(T)$ and $MR(T)$ are observed, have been determined. Conclusions have been made as for the FM phase nuclei shape in the films under consideration.

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Динаміка трансформації магнітних та електричних параметрів у тонких плівках заміщених натрієм манганітів лантану

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Досліджено динаміку трансформації магнітних і електричних параметрів у тонких плівках заміщених натрієм манганітів лантану, характерною особливістю яких є широка температурна область співіснування феромагнітної і парамагнітної фаз. Виявлено, що аномалії на температурних залежностях намагніченості, електричного опору та магнітоопору зсунуті один відносно одного на відміну від монокристалічних зразків заміщених манганітів, в яких такі аномалії спостерігаються практично при одній і тій же температурі. Базуючись на даних магнітних вимірювань і результатах теоретичних розрахунків, обчислено залежність об'ємної частки феромагнітної фази V_{FM} від температури. Знайдено конкретні значення V_{FM}, при яких спостерігаються максимуми на температурних залежностях електричного опору та магнітоопору. Зроблено висновки щодо форми зародків феромагнітної фази у плівках, що досліджуються.